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最終頁に続く

(54) 【発明の名称】 生分解性プラスチック材料製発泡製品とその製造方法

(57) 【要約】

【構成】 生分解性プラスチック材料製発泡製品を、熱可塑性澱粉 50～95wt%、少なくとも1つの熱可塑性ポリマー 0.5～45wt%と水 2～20wt%とからなる材料より構成される密度 0.1～0.003g/cm³ と直径 0.5～10mmの大きさを有する発泡粒子をその粒子表面を粒子の均質接触で相互に安定化され得るように改質するため、熱処理及び/又は少なくとも1つの核剤で処理し、凝集することにより製造する。

【特許請求の範囲】

【請求項1】 熱可塑性澱粉50～95wt%と、少なくとも1つの熱可塑性ポリマー 0.5～45wt%と、水 2～20wt%とからなる材料より構成される粒子で、0.1～0.003g/cm³の範囲の密度と0.5～10mmの範囲の直径の大きさを有する凝集発泡粒子から構成される生分解性プラスチック材料製発泡製品。

【請求項2】 熱可塑性ポリマーが、ポリ（ビニルアルコール）、オレフィンモノマーとビニルアルコール、ビニルアセテート、アクリル酸及びメタクリル酸から選択されるモノマーとのコポリマー、脂肪族ポリエステル及び脂肪族ポリアミドから選択される請求項1の発泡製品。

【請求項3】 オレフィンモノマーが、エチレンである請求項2の発泡製品。

【請求項4】 脂肪族ポリエステルが、ポリカプロラクトン、ポリ（ブチレンスクシネート）及びそれらのコポリマーから選択される請求項2の発泡製品。

【請求項5】 発泡粒子を構成する材料が、少なくとも1つの核剤0.005～5wt%からなる請求項1～4のいずれか1つの発泡製品。

【請求項6】 核剤が、タルク、炭酸カルシウム、砂糖大根の処理から生ずるイーストシエル、乾燥、粉碎及び粉末化した砂糖大根の葉肉、木粉、セルロース粉末から選択される請求項5の発泡製品。

【請求項7】 発泡粒子を構成する材料が、少なくとも1つのスリップ剤及び／又は親水性／親油性バランス指数（HLB）が3～25の範囲の分散剤0.01～5wt%からなる請求項1～6のいずれか1つの発泡製品。

【請求項8】 発泡粒子を構成する材料が、少なくとも1つの可塑剤0.5～20wt%からなる請求項1～7のいずれか1つの発泡製品。

【請求項9】 可塑剤が、グリコール、ソルビトール、マンニトール、エリトリトール、低分子量ポリ（ビニルアルコール）、前記化合物のオキシエチレート及びオキシプロピレート誘導体、及び尿素から選択される請求項8の発泡製品。

【請求項10】 熱可塑性澱粉50～95wt%と少なくとも1つの熱可塑性ポリマー 0.5～45wt%からなる材料と、水 2～20wt%から構成され、0.1～0.003g/cm³の範囲の密度と0.5～10mmの直径の範囲の大きさの発泡粒子を、その粒子の表面を、これらを相互の相互均質接触させたとき、互いに安定的に相互作用させるよう改質するため、熱処理及び／又は少なくとも1つの被覆剤との処理に付し、かつ次いで、その発泡粒子を凝集させるのに十分な長い時間、互いに均質接触を保持することから

i. 塩及び／又は添加物を添加してもよい液体の水、又は気体の水、

ii. 天然又は合成、高分子又は単量体の物質の水性の液、懸濁液及び／又はエマルジョン、又は溶融状態にある前記物質、

iii. 十分に高い湿潤力を持つ溶媒、

iv. 前記溶媒中での、天然又は合成、高分子又は単量体の物質の溶液、懸濁液及び／又はエマルジョン

v. 融点が130℃以下、好ましくは90℃以下のポリマー。

【請求項12】 被覆剤が、ポリ（ビニルアセテート）である請求項11の製造方法。

【請求項13】 液状物質の蒸発及び／又は被覆剤に有する単量体物質の重合化を促進させるために、粒子相互均質接触さす工程の前に、同時又は後で行ってもよい加熱処理及び／又は通気処理工程からなる請求項1～12のいずれか1つによる製造方法。

【請求項14】 得られた発泡製品を乾燥、湿潤又は節された条件のもとで後乾燥処理を行うことからなる請求項10～13のいずれか1つによる製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は生分解性プラスチック材料製発泡製品とその製造法に関する。

【0002】

【従来の技術】特に保護的な包装に用いられる発泡材の利用分野において、発泡ポリスチレンの代替としてより強い生分解性の要件を満たす材料の必要性が求められている。この目的に、従来、澱料系材料の使用が増された。

【0003】ヨーロッパ特許第 A-0,087,847号は、澱又は澱粉を含む基材を水10～30wt%と発泡剤の存在下押出圧で加熱し、次いで押出して澱料系発泡製品の製造法を開示している。ヨーロッパ特許第 A-0,375,831号は、良好な機械的及び独立気泡構造特性を有する高アミース澱粉で構成される発泡製品を開示している。この発泡製品は水の存在下、150～250℃の範囲の温度押出し、恐らく熱成形処理をさせて製造される。

【0004】国際特許出願第WO 91/02,023号は、澱粉を含む組成物とエチレン、ビニルアルコール及びエチレン-アクリル酸コポリマーから選択される合成高分子を台酸と発泡剤としての炭酸水素ナトリウムの存在下で出成形する生分解性プラスチック材料の発泡製品を開示している。しかしながら、従来法による操作では、前記形状あるいは厚さを持つ発泡製品の製造は、困難な問題である。更に、得られる発泡製品は一般に十分な

な弾性と圧縮性を持つ生分解性プラスチック材料の発泡製品の提供である。ゆえに、本発明の目的は、 $0.1 \sim 0.03 \text{ g/cm}^3$ の範囲の密度、及び直径 $0.5 \sim 10 \text{ mm}$ の範囲の大きさを有する発泡粒子によって構成され、粒子が次の材料によって構成される生分解性プラスチック材料製発泡製品である。

【0006】・熱可塑性澱粉 $50 \sim 95 \text{ wt}\%$ 、好ましくは $60 \sim 95 \text{ wt}\%$

・少なくとも1つの熱可塑性ポリマー $0.5 \sim 45 \text{ wt}\%$ 、好ましくは $2 \sim 35 \text{ wt}\%$

・水 $2 \sim 20 \text{ wt}\%$ 、好ましくは $5 \sim 17 \text{ wt}\%$

本発明の発泡製品を構成する発泡粒子は、好ましくは、 $0.05 \sim 0.005 \text{ g/cm}^3$ の範囲の密度、及び好ましくは $1 \sim 5 \text{ mm}$ の範囲の大きさを持つ。

【0007】前記発泡粒子は独立気泡構造を持つ。それらは種々の形状、特に実質上球の形状を持ち得る。上記発泡粒子の組成物中の一つあるいはそれ以上の熱可塑性ポリマーの存在は、組成物の熔融強度の改良を可能にし、発泡製品とともに良好な弾性と低感湿性を与え得る。

【0008】前記発泡粒子の成分として使用し得る熱可塑性澱粉は、天然澱粉、好ましくはコーンスターチ又はじゃがいも澱粉、又は高アミロース澱粉等級、好ましくはアミロースを30%以上含むもの、及びろう澱粉等級である。更に、物理的及び化学的に改質された澱粉として、 $0.1 \sim 2$ の範囲の置換率を持つエトキシレート澱粉、オキシプロピレート澱粉、アセテート澱粉、ブチレート澱粉、プロピオネート澱粉；カチオン澱粉、酸化澱粉、架橋澱粉、ゲル化澱粉、“V”-タイプ複合体を与え得るポリマー、例えば、エチレン-ビニルアルコール(EVOH)、エチレン-アクリル酸(EAA)、エチレン-無水マレイン酸コポリマー、エチレン-エチルアクリレート-無水マレイン酸ターポリマーで複合した澱粉；グラフト化澱粉、分解澱粉、破壊澱粉が使用できる。

【0009】天然の澱粉は、約 $9 \sim 16 \text{ wt}\%$ の水を含み、通常、予備的な脱水に供することなしに使用される。発泡粒子の組成物に使用し得る熱可塑性ポリマーは次から選択される。

1. $1 \sim 2.5$ の範囲の置換率を持ち、可塑化されてもよいセルロースアセテート又はセルロースブチレート、アルキルセルロース、ヒドロキシアルキルセルロース、カルボキシアルキルセルロース、特にメチルセルロースのような天然産ポリマー、改良あるいは未改良の、特にセルロース誘導体、及び更にキトサン、セラック、又はカゼイン及びカゼイネート、

コールから誘導されるポリエステル、例えば、

・ポリ(エビシロン-カプロラクトン)、又はそのラフト又はブロックコポリマー、カプロラクトンオリゴマーあるいはポリマーと芳香族又は脂肪族イソシアネートの反応生成物、

・乳酸又はラクチドのポリマー、グリコール酸又はグリコリドのポリマー、乳酸とグリコール酸のコポリマー、

10 ・ポリヒドロキシブチレート又はポリヒドロキシブチレート-バレレート、

・ポリアルキレンスクシネート及び、特にポリエチレンスクシネート又はポリブチレンスクシネート、ポリエレンアジベート又はポリブチレンアジベート、ポリエレンセバケート又はポリブチレンセバケート、ポリエレンアゼレート又はポリブチレンアゼレート、ポリエレンブチレート又はポリブチレンブチレート及びこれらのコポリマー(脂肪族又は芳香族イソシアネート共重合化できる、更にこれらは連鎖延長剤で分子量を大きくしてもよい)、

20 iii. アミロースと“V”-タイプ複合体の形成し得るポリマー、又は疎水性配列を介在した親水基を含むポリマー、例えば、

・エチレン単位を $50 \text{ wt}\%$ まで好ましくは $10 \sim 44 \text{ wt}\%$ のエチレン-ビニルアルコールポリマー、酸化されたエチレン-ビニルアルコールコポリマー、又は脂肪酸でオキシ化、又はポリカプロラクトンでグラフト化、又はメタリルモノマーのアクリル及び/又はビリジニウムで置換したエチレン-ビニルアルコールコポリマー、

30 ・部分的に加水分解されてもよいエチレン-ビニルアセテートコポリマー、

・エチレン-アクリルエステルコポリマー、

・エチレン-アクリル エステル-無水マレイン酸又はエチレン-ビニルアセテート-グリシジル メタクリルターポリマー、

・アクリル酸、メタクリル酸、クロトン酸、イタコン酸、無水マレイン酸のような不飽和酸とのエチレンコポリマー、特にアクリル酸から誘導される単位を $5 \sim 50 \text{ mol}\%$ 好ましくは $10 \sim 30 \text{ mol}\%$ 含むエチレン-アクリルコポリマー、

40 ・全体的又は部分的に加水分解されてもよいビニルアセテートと、アクリル酸、メタクリル酸、クロトン酸又はイタコン酸とのエチレンターポリマー、

・脂肪族の 6-6、6-9又は12ポリアミド、脂肪族ポリウレタン、ランダム又はブロックポリウレタン-ポリウレタン、ポリウレタン-ポリエステル、ポリウレタン-エーテル、ポリアミド-ポリエステル、ポリアミド-

化又はそれらの融点を低下させるために改良された、あるいは硼酸、ボレート、ホスフェートのようなゲル化剤を含んでもよいポリ(ビニルアルコール)；ビニルピロリドン又はスチレンとのビニルアセテートコポリマー（種々の加水分解率）、ポリエチルオキサゾリン、ポリビニルピリジン。

【0010】好ましい熱可塑性ポリマーは、ポリ(ビニルアルコール)、オレフィンモノマー、好ましくはエチレンと、ビニルアルコール、ビニルアセテート、アクリル酸及びメタクリル酸から選択されるモノマーとのコポリマー、ポリカプロラクトン、ポリ(ブチレンスクシネート)及びそれらのコポリマーのような脂肪族ポリエステル、及び脂肪族ポリアミドである。

【0011】本発明の発泡製品を構成する発泡粒子は、好ましくは核剤を含む。発泡材料中のこのような核剤の量は、0.005～5wt%、好ましくは0.05～3wt%、より好ましくは0.2～2wt%の範囲からなる。用いることのできる核剤は、例えば無機化合物ではタルク（珪酸マグネシウム）、炭酸カルシウム等、あるいはシリラン及びチタネート等である。

【0012】更にテンサイ加工のイーストシェル(yeast shells)、乾燥、粉碎及び粉末化したテンサイの葉肉、木粉、セルロース粉末等の有機充填剤を用いることができる。核剤は、発泡粒子を作る混合物に加えることができ、あるいは代りに、マスターバッチとしての発泡粒子に加えることができる。後者の場合、マスターバッチは、1つ又はそれ以上の充填剤を10～50%含めることができる。

【0013】更に発泡粒子は、1つ又はそれ以上のスリッパ剤及び/又は3～25の範囲、好ましくは6～20の範囲の親水性／親油性バランス指数(HLB)を持つ分散剤を含めることができる。使用する際、これらの添加剤は0.01～5wt%、好ましくは0.1～3wt%の範囲の量を与えることができる。発泡粒子は1つ又はそれ以上の可塑性剤も含めることができる。使用する際、前記可塑性剤は、0.5～20wt%、好ましくは0.5～5.0wt%の範囲の量を与えることができる。

【0014】用いることができる可塑性剤は、例えば国際特許出願第 WO92/14,782号で開示されており、その内容をここに導入する。特に可塑性剤として使用に適するものは、グリコール、ソルビトール、マンニトール、エリトリトール、低分子量ポリ(ビニルアルコール)、それらのオキシエチレート及びオキシプロピレート誘導体、及び、更に尿素である。

【0015】更に発泡粒子は、1つ又はそれ以上の難燃剤を含めることができ、発泡粒子を作る混合物に加える

図の量を与える。

【0016】難燃剤はリン含有物、硫黄含有物、又はロゲン化合物から導かれる化合物から選択される。例えば、トリフェニルホスフェート、トリブチルホスフェート、トリクレジルホスフェート、トリブトキシフェニルホスフェート、メラミンピロホスフェート、アンモニウムホスフェート、エチレンジアミン、グアニジウムホスフェート、テトラブロモフタル酸無水物、ハロゲン化パラフィン、臭化率の異なるジフェニルオキサリド、アンモニウムスルフェート、アンモニウムスルファメート等が所望の目的に適する。アンモニウムスルファメート、アンモニウムスルファメート、アンモニウムホスフェート、グアニジウムホスフェート、及び、ミンピロホスフェートが特に有利である。

【0017】他の用いることのできる難燃剤は水酸アルミニウム、三酸化アンチモン、過硫酸アンモニウム、アンモニウムオクタモリブデート等である。特別の表面について、細菌類に対する忌避物質の存在が必要なきは、それらは発泡粒子を作る混合物に加えたり、又は活性物質含有マイクロカプセルとして、又は特に核剤及び/又は難燃剤と組合わせてマスターバッチとして発泡粒子に加えることができる。

【0018】この目的にN、N-ジエチル- α -トリミド、ジエチルフェニルアセタミド、2-デカナール塩化アンモニウム、塩素酸カリウム、テルペノイド、クロヘキシミド、ジグアニジノアザヘプタデカン等を用いることができる。テルペノイド、及び特にメントール及びリモネンが好ましい。使用の際、それらの忌避剤は、0.1～5wt%、好ましくは1～3wt%の範囲の量を与える。

【0019】本発明の発泡製品を構成する発泡粒子は、澱粉系組成物の押出の方法によって製造でき、単軸又は二軸スクリー押出機で行える。このような押出工程は5～20wt%の範囲の量の水の存在下で行ない、組成物に含まれる澱粉は破壊する。しかしながら、水の含有量は、ノズルでの全含水量が5～20wt%の範囲であるように換気機構によって制御されるべきである。

【0020】代りに、顆粒は公知の方法によりあらかじめ破壊した熱可塑性澱粉の顆粒を使うことができる。例えば、国際特許出願第 WO92/02,363号及び第 WO92/128号の内容を本明細書に導入する。前記の押出工程は一般的に150～250℃の範囲の温度で、一般的に20秒から15分の滞在時間で行われる。押出ヘッド下流のノズル切断（ペレット化）は、高速で行われ、溶融材料が化していない時に切断され、得られた粒子（ペレット）はほとんど球状の粒子になる。押出ヘッドの切断値は

次いでヘッド切断、又は大寸法の顆粒の粉碎によって得ることができる。これらの未発泡粒子を40〜200℃の範囲の温度で、材料中に含まれる水と平衡な水分の存在下で、2〜100バールの範囲の圧力に付し、次いで急速の減圧に供する。

【0022】発泡粒子のまた別の製造方法は、前記の未発泡粒子をマイクロ波による熱処理に供することよりなる。本発明の生分解性プラスチック材料製発泡製品は、前記材料の発泡粒子の凝集工程により製造できる。熱可塑性澱粉50〜95wt%好ましくは60〜95wt%と、少なくとも1つの熱可塑性ポリマー0.5〜45wt%好ましくは2〜35wt%からなる材料と、水2〜20wt%好ましくは5〜17wt%から構成され、0.1〜0.005g/cm³の範囲の密度と0.5〜10mmの直径の範囲の大きさの発泡粒子を、その粒子の表面を、これらを相互均質接触させたとき、互いに安定的に相互作用させるよう改質するため、熱処理及び／又は少なくとも1つの被覆剤との処理に付し、かつ次いで、その発泡粒子を凝集させるのに十分な長い時間、互いに均質接触を保持することからなる生分解性プラスチック材料から作られた発泡製品の製造法である。

【0023】発泡粒子の良好なレジリエンス特性は、粒子が均質接触にある時、どのようなコラプシング（気泡破壊）現象にも耐え得る。本発明による方法で用いることのできる被覆剤は、例えば、

- i. 塩及び／又は添加物を添加してもよい液体の水、又は気体の水、
- ii. 天然又は合成、高分子又は単量体の物質の水性の溶液、懸濁液又はエマルジョン、又は溶融状態による前記物質、
- iii. 十分に高い湿潤力を持つ溶媒、
- iv. 前記溶媒中での、天然又は合成、高分子又は単量体の物質の溶液、懸濁液又はエマルジョン、
- v. 融点が130℃以下、好ましくは90℃以下のポリマー。

【0024】本発明の方法で水性の溶液、懸濁液又はエマルジョンに用いることができる被覆剤の例は

- ・ポリ（ビニルアセテート）、
- ・ポリ（ビニルブチレート）、
- ・ビニルアセテート又はビニルブチレートとビニルエステル、アクリレート、メタクリレート、アリル誘導体、
- ・ピリジニウム塩、アクリロニトリル、アクリルアミド、
- ・ビニルピロリドン、ビニルピリジン、ビニルイミダゾルから選択される1つ又はそれ以上の単量体とのコポリマーで、これらは一部又は全部が加水分解されていてよい。
- ・ポリカプロラク톤のような脂肪族ポリエステル又は

- を混合してもよいポリ（ビニルアルコール）、
- ・アセタール化、エーテル化、又はエステル化により質されたポリ（ビニルアルコール）
- ・ポリ（ビニルアセテート又はスチレン）とのポリ（ビニルアルコール）のブロックコポリマー、
- ・脂肪酸キャップのポリ（ビニルアルコール）、
- ・ポリオキシエチレン及び／又はポリオキシプロピルとグラフト化したポリ（ビニルアルコール）、
- ・あらゆる起源の天然澱粉、ヒドロキシアルキル化、
- ・チオン性、酸化、架橋、加水分解された澱粉、又はエ
- ・テル、エーテル及び／又はリン酸基で改質された澱粉
- ・カゼイン及びカゼイネート、
- ・アルキルセルローズ、ヒドロキシアルキルセルロー及びセルローズエステル、例えば可塑化及び／又はカ
- ・ロラク톤のような脂肪族エステルで改質されてもよ
- ・セルローズアセテートとカルボキシメチルセルロー
- ・ス、
- ・天然ゴムラテックス、
- ・アクリルアミド、アクリロニトリル、スチレン又は
- ・クリルエステルとグラフト化されてもよいアラビヤ
- ・コのような天然ゴム（植物性ヒドロコロイド）、
- ・アルギン酸、アルギネート、アビエチン酸、ロジン
- ・脂、寒天、グヤガム、カラギーニン、キサンタンガム
- ・ブルラン、キトサン、セラック、動物ゼラチン、プロ
- ・テイン、乳化剤、分散剤、充填剤、
- ・ポリ（アクリル酸）、エチレン／アクリル酸コポリ
- ・マー、アクリルアミド／アクリル酸コポリマー、ポリ
- ・チレンスルホン酸）から誘導されるイオン性ポリマー
- ・アンモニウム又はナトリウム塩、
- ・一般に脂肪族の特性のホモ及びコポリマー、特にオ
- ・カプロラクトン、ポリ（乳酸）、ポリ（ヒドロキシ
- ・レートバレート）、ポリ（ブタンジオールスクシネ
- ・ート）のようなポリウレタン、ポリアミド、ポリエステル
- ・、及び部分的に置換された多官能性アルコールと
- ・これらのコポリマー。

【0025】上記に挙げた物質の中で、ポリ（ビニルアセテート）は特に本発明による方法で被覆剤としての用に適する。本発明の発泡製品の製造法は、液状物質蒸発及び／又は被覆剤に含有した単量体物質の重合（促進のため、粒子を均質接触さす工程の前に、同時に

【0026】得られる発泡製品は、更に後乾燥処理にすることが適する。この後乾燥処理は、残留する水又は溶媒を除去させるもので、乾燥、湿潤又は調節された条件のもとで行うことができる。ポリマー化可能な単量体からなる被覆剤の場合、前記後処理は、重合反応及び／

0.05～3wt%の範囲の、好ましくは0.1～2wt%の範囲の、より好ましくは0.2～1wt%の範囲の量で乳化剤及び／又は増粘剤を含めることができる。用いることができる乳化剤は、例えば3～25、好ましくは5～20の範囲の親水性／親油性バランス指数(HLB)を持つ界面活性剤である。特に有効な界面活性剤には、ポリオキシエチレン又はポリオキシプロピレンを脂肪酸で直接エステル化したもの、例えばラウリン酸、パルミチン酸もしくはステアリン酸でエステル化したポリオキシエチレン

(4～20モル)、又はポリオキシエチレン化糖を脂肪酸でエステル化したもの、例えば1～6モルの脂肪酸でエステル化したオキシエチル化(4～20モル)ソルビトール、のようなポリオキシエチレン又はポリオキシプロピレンから誘導のものがある。更に、用いることができる界面活性剤は、オキシエチル化ノニルフェノール、ラノリンエーテル及びエステル、トリエタノールアミンオレエート、脂肪酸のポリグリセロールエステル、例えばステアリルアルコール、セチルアルコール又はコレステロールのような脂肪族アルコールとのポリオキシエチレンエーテル、PEG-牛脂アミド、PEG-ヒマシ油である。

【0028】用いることができる増粘剤は、例えばカルボキシメチルセルロースナトリウム、メチルセルロース、天然ゴム、粘土等である。好ましい態様によれば、本発明の方法は、図1に示されるような装置の形式を用いることにより好適に行なうことができる。図1において、引用番号1、3及び9はスライド可能な分離壁を示し、2、4及び10で示される開閉系によって各々、圧縮空気で動作する。

【0029】分離壁1を開け、発泡粒子を計量室5に充填する。次いで分離壁1を閉め、分離壁3を開け、粒子を噴霧室6に落とし入れる。次いで分離壁3を閉め、被覆剤を含む噴霧器7の動作を開始し、噴霧室6が被覆剤で飽和するのに十分な長い時間動作させる。ここで噴霧器7を停止させ、分離壁9を開け、粒子をダクト11に落とし入れる。モールドの各々雄と雌の部分14及び15をこのような位置に保持する。その間の空気間隔16の幅はペレットの直径より小さい。分離壁9を閉め、ピストン12により粒子をモールド側に供給し、それらに圧力をかける。モールドを最後にピストン17により開

け、得られる製品を回収する。
【0030】別の好ましい態様によれば、本発明の方法は、発泡ポリスチレン粒子を焼結するのに用いたと同様の装置(通気開孔をもつモールド)の成型室に供給経路を直接向け、発泡粒子を被覆剤との処理に付すことにより好適に行うことができる。最後に、被覆剤は、発泡粒

子に供給することができる。

【0031】次の実施例は例示目的で与えるもので、発明を限定するものではない。

特性付け

レジリエンス試験

この試験は変形をもたらす荷重を加えた後、その初期状に回復する材料性能を測定するものである。

【0032】直径125mm及び高さ150mmの円筒容器に発泡粒子を充填し、荷重計のフラットセンサーを押し込み、25mm/分の速度で動作させる。センサーは円筒底の33%で粒子を圧し、次いで出発位置にセンサーを戻す。1分後、センサーで第2回目の粒子圧縮操作を第1回目と同様の操作で行なう。a%の数値で報告されるレジリエンス値は第1回目の圧縮動作の荷重を第2回目圧縮動作の荷重で割った比の100倍である。

密度

Dapp(kg/m³) 粒子51の重量から算出した発泡粒子嵩(見掛け)密度、

Dbulk(kg/m³) 個々の発泡粒子の比重密度、

20 Dexp(kg/m³) 発泡製品の比重密度。

【0033】

【実施例】

実施例1

混合物を以下の組成物で作った。

・ジャガイモ澱粉 75wt%

・加水分解率86%のポリ(ビニルアルコール) 10wt%

・水 15wt%

この組成物を直径(d)30mm、長さ(d)の比[(L)/(d)]30の二軸スクリー押出機AP-2030に供給した。操作条件は以下のようにした。

【0034】・スクリー回転速度 150rpm

・温度勾配 69°C/100°C/180°C/170°C/155°C

・押出量 10kg/時間

全含水率が約14%に保持されるように調整した。得られたペレットを平均粒子径約1.5μmのタルク0.5%と、直径(d)40mm、[(L)/(d)]28の単軸スクリー押出機ex 08Cに供給し、直径(d)0.8mm[(L)/(d)]1以下の4つのノズルの押出ヘッドを装着した。

40 【0035】操作条件は以下のようにした。

・スクリー回転速度 40rpm

・温度勾配 80°C/120°C/190°C/190°C/200°C

・押出量 52kg/時間

・ヘッド切断刃回転速度 4000rpm

発泡材料のペレットが得られた。特性を表1に示す。

【0036】

11

2	3.0	10
3	3.2	14
4	3.3	21
5	3.2	16
6	3.5	21

実施例2

操作方法は実施例1と同様とし、以下の組成物の混合物を使用した。

【0037】・じゃがいも澱粉 64wt%

・加水分解率99.8%、分子量(Mw)70,000、エチレン単位を44モル%含むEVOH 25wt%

・水 10wt%

・グリセロールモノオレート 1wt%

ペレット中の含水量は約10%であった。発泡ペレットの特性を表1に示す。

実施例3

操作方法は実施例1と同様とし、以下の組成物の混合物を使用した。

【0038】・じゃがいも澱粉 78wt%

・加水分解率99.8%、分子量70,000、エチレン単位を44モル%含むEVOH 7wt%

・加水分解率86%のポリ(ビニルアルコール) 8wt%

・水 5wt%

・グリセロールモノオレート 1wt%

ペレット中の含水量は約12%であった。発泡ペレットの特性を表1に示す。

実施例4

操作方法は実施例1と同様とし、以下の組成物の混合物を使用した。

【0039】・じゃがいも澱粉 68wt%

・ポリカプロラクトン(UC PCL 787) 10wt%

・カプロラクトン-ウレタンブロックコポリマー(Pellthane 2102-85AE9) 5wt%

・水 15wt%

・グリセロールモノオレート 1wt%

ペレット中の含水量は約10%であった。発泡ペレットの*

12

*特性を表1に示す。

実施例5

操作方法は実施例1と同様とし、以下の組成物の混合物を使用した。

【0040】・じゃがいも澱粉 75wt%

・アクリル単位を20モル%を含むエチレン-アクリルコポリマー(ダウケミカル社製) 10wt%

・水 15wt%

ペレット中の含水量は約10%であった。発泡ペレット特性を表1に示す。

実施例6

操作方法は実施例1と同様とし、以下の組成物の混合物を使用した。

【0041】・じゃがいも澱粉 75wt%

・カプロラクトン20%で可塑化した置換率 2.5のセルースアセテート 10wt%

・水 15wt%

ペレット中の含水量は約12%であった。発泡ペレット特性を表1に示す。

実施例7

図1に示す装置の計量室5、容置21に実施例3で得られた発泡粒子を供給した。

【0042】次いで、上記の方法によってポリ(ビニルアセテート)50%を含むヴィナビル(Vinavil)NFエマルジョン(Emchem Synthesis)で処理し、噴霧7により微粒化した。得られた製造物を23℃、相対湿度(RH)30%に制御した反応室に15時間、後乾燥処理を行った。

【0043】発泡製品の特性を表2に示す。

【0044】

【表2】

実施例	モールド温度 (°C)	D exp (kg/m ³)	縦収縮 (%)
7	20	50	3
8	20	43	3.5
9	20	40	4
10	20	36	5
11	20	25	1
12	20	60	23
13	30	46	12

実施例8実施例9

実施例10

操作方法は実施例7と同様とした。この時ヴィナビル (Vinavil) NPCエマルジョン (Enichem Synthesis) の水との希釈を 1/2 (水/Vinavil) とした。

【0047】発泡製品の特性を表2に示す。

実施例11

操作方法は実施例10と同様とし、異なる点は発泡ベレットに実施例2から得られたものを使用した。発泡製品の特性を表2に示す。

実施例12

操作方法は実施例10と同様とし、異なる点は発泡ベレットに実施例1から得られたものを使用した。

【0048】発泡製品の特性を表2に示す。

実施例13

操作方法は実施例10と同様とし、異なる点は後乾燥処理を23℃、RH55%に制御した反応室で15時間行った。発泡製品の特性を表2に示す。

【0049】

【発明の効果】本発明によれば、良好な機械的特性、特に良好な弾性と圧縮性を持つ生分解性プラスチック材料*20

*製発泡製品とその製造方法が提供される。

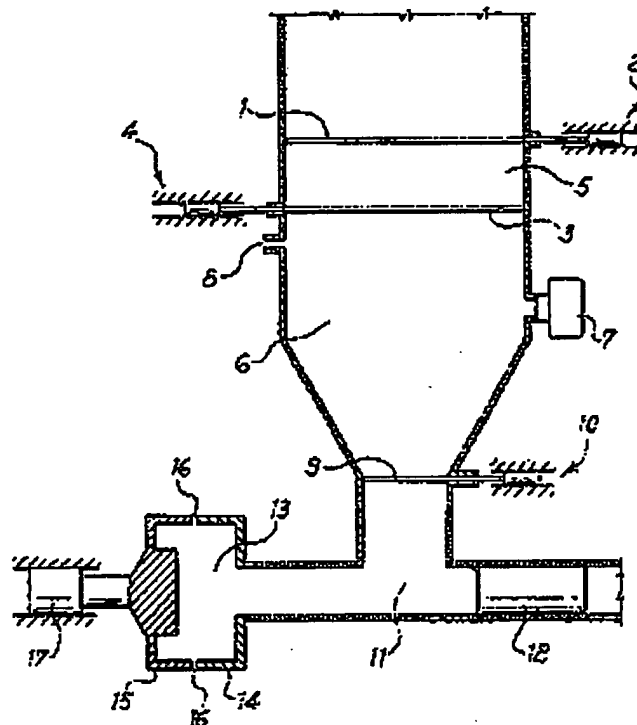
【図面の簡単な説明】

【図1】本発明の製造法を示す装置の概略図である。

【符号の説明】

- | | |
|----|-------|
| 1 | 分離壁 |
| 2 | 開閉系 |
| 3 | 分離壁 |
| 4 | 開閉系 |
| 5 | 計量室 |
| 6 | 噴霧室 |
| 7 | 噴霧器 |
| 9 | 分離壁 |
| 10 | 開閉系 |
| 11 | ダクト |
| 12 | ピストン |
| 13 | 成形室 |
| 14 | 雄モールド |
| 15 | 雌モールド |
| 16 | 空気間隙 |
| 17 | ピストン |

【図1】



から公知の分解法で得ることができる。更に、熱可塑性澱粉は、物理的及び化学的に改質された澱粉；0.1～2の範囲の置換率を持つエトキシレート澱粉、オキシプロピレート澱粉、アセテート澱粉、ブチレート澱粉、プロピオネート澱粉；カチオン澱粉、酸化澱粉、架橋澱粉、ゲル化澱粉、“V”-タイプ複合体を与え得るポリマー、例えば、エチレン-ビニルアルコール（EVOH）、エチレン-アクリル酸（EAA）、エチレン-無水マレイン酸コポリマー、エチレン-エチルアクリレート-無水マレイン酸ターポリマーで複合した澱粉；グラフト化澱粉、分解澱粉から得ることができる。

【手続補正2】

【補正対象書類名】明細書

【補正対象項目名】0029

【補正方法】変更

【補正内容】

【0029】分離壁1を開け、発砲粒子を計量室5に充填する。次いで分離壁1を閉め、分離壁3を開け、粒子を噴霧室6に落とし入れる。次いで分離壁3を閉め、被覆剤を含む噴霧器7の動作を開始し、噴霧室6が被覆剤で飽和するのに十分な長い時間動作させる。通気孔8は噴霧室6が加圧されるのを防ぐ。ここで噴霧器7を停止させ、分離壁9を開け、粒子をダクト11に落とし入れる。モールドの各々雄と雌の部分14及び15をこのような位置に保持する。その間の空気間隙16の幅はベレットの直径より小さい。分離壁9を閉め、ピストン12*

*により粒子をモールド側に供給し、それらに圧力をかける。モールドを最後にピストン17により開け、得る製品を回収する。

【手続補正3】

【補正対象書類名】明細書

【補正対象項目名】符号の説明

【補正方法】変更

【補正内容】

【符号の説明】

- 1 分離壁
- 2 閉関係
- 3 分離壁
- 4 閉関係
- 5 計量室
- 6 噴霧室
- 7 噴霧器
- 8 通気孔
- 9 分離壁
- 10 閉関係
- 11 ダクト
- 12 ピストン
- 13 成形室
- 14 雄モールド
- 15 雌モールド
- 16 空気間隙
- 17 ピストン

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CLAIMS

[Claim(s)]

[Claim 1] Thermoplastic starch 50 – 95wt% and at least one thermoplastic polymer 0.5 – 45wt% and water. At the particle which consists of ingredients which consist of 2 – 20wt%, it is 3 0.1 to 0.003 g/cm. Consistency of the range. Foaming product made from biodegradability plastic material which consists of condensation foaming particles which have the magnitude of the diameter of the range of 0.5–10mm.

[Claim 2] The foaming product of claim 1 with which a thermoplastic polymer is chosen from a copolymer, aliphatic series polyester, and an aliphatic series polyamide with the monomer chosen from Pori (vinyl alcohol), an olefin monomer and vinyl alcohol, vinyl acetate, an acrylic acid, and a methacrylic acid.

[Claim 3] The foaming product of claim 2 whose olefin monomer is ethylene.

[Claim 4] The foaming product of claim 2 with which aliphatic series polyester is chosen from the poly caprolactone, Pori (butylene succinate), and those copolymers.

[Claim 5] Any one foaming product of claims 1–4 with which the ingredient which constitutes a foaming particle consists of at least one nucleating additive 0.005 – 5wt%.

[Claim 6] The foaming product of claim 5 with which a nucleating additive is chosen from talc, a calcium carbonate, the yeast shell produced from processing of a sugar cane, desiccation, grinding and the mesophyll of the sugar cane which carried out disintegration, wood flour, and cellulose powder.

[Claim 7] At least one slipping agent, and/or a hydrophilic property / oleophilic balance characteristic (HLB). Any one foaming product of claims 1–6 which consists of dispersant [of the range of 3–25] 0.01 – 5wt%. [the ingredient which constitutes a foaming particle]

[Claim 8] The ingredient which constitutes a foaming particle is at least one plasticizer. Any one foaming product of claims 1–7 which consists of 0.5 – 20wt%.

[Claim 9] The foaming product of claim 8 with which a plasticizer is chosen from a glycol, a sorbitol, a mannitol, an erythritol, low-molecular-weight Pori (vinyl alcohol), the oxy-ethylate of said compound, an oxy-PUROI rate derivative, and a urea.

[Claim 10] Thermoplastic starch 50 – 95wt% and at least one thermoplastic polymer. The ingredient which consists of 0.5 – 45wt%, water it consists of 2 – 20wt% -- 0.1 – 0.003 g/cm³. Consistency of the range. When mutual carries out mutual homogeneity contact of these for the front face of the particle, the foaming particle of the magnitude of the range of 0.5–10mm diameter. In order to reform so that an interaction may be carried out stably mutually, heat treatment and/or processing with at least one coating are given. Subsequently. Sufficient long time amount for making the foaming particle condense, the manufacture approach of the foaming product made from the biodegradability plastic material which consists of holding homogeneity contact mutually.

[Claim 11] The manufacture approach of claim 10 chosen from the following coating.

i. Water of the liquid which may add a salt and/or an additive, or gaseous water, ii. The solution, the water suspension, and/or the water emulsion of nature or composition, a giant molecule, or the matter of a monomer, or said matter by the melting condition and iii. -- a solvent with wetting power high enough, and iv. Nature or composition--in said solvent, giant-molecule or solution [of the matter of a monomer], suspension, and/or emulsion v. The melting point 130 degrees C or less -- desirable -- polymer 90 degrees C or less.

[Claim 12] The manufacture approach of claim 11 that coating is Pori (vinyl acetate).

[Claim 13] The manufacture approach by any one of the claims 10-12 which consist of the heat-treatment and/or aeration down stream processing which may perform a particle before a mutual homogeneity contact **** process in coincidence or the back in order to promote polymerization-ization of the monomer matter contained in evaporation and/or coating of the liquefied matter.

[Claim 14] The manufacture approach by any one of the claims 10-13 which consist the obtained foaming product of performing back desiccation processing under desiccation, humidity, or the conditions that were adjusted.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the foaming product made from biodegradability plastic material, and its manufacturing method.

[0002]

[Description of the Prior Art] In the field of the invention of the charge of foam especially used for a protective package, the need for the ingredient which satisfies the requirements for stronger biodegradability as an alternative of form polystyrene is searched for. The activity of a **** system ingredient was conventionally proposed by this object.

[0003] European Patent ** No. A-0,087,847 heats the base material containing starch or starch with extrusion pressure under existence of water 10 - 30wt% and a foaming agent, subsequently extrudes it, and is indicating the manufacturing method of a starch system foaming product. European Patent ** No. A-0,375,831 is indicating the good foaming product which consists of mechanical and high amylose starch showing a closed cell structure property. These foaming products are extruded at the temperature of the bottom of existence of water, and the range of 150 to 250 degree C, probably carry out thermoforming processing, and are manufactured.

[0004] the [international patent application] -- WO 91 / No. 02 or 023 are indicating the foaming product of the biodegradability plastic material which carries out extrusion molding of the synthetic macromolecule chosen from the constituent containing starch, ethylene, vinyl alcohol, and an ethylene-acrylic-acid copolymer under existence of the sodium hydrogencarbonate as polyacid and a foaming agent. However, manufacture of the foaming product which has a complicated configuration or thickness in actuation by the conventional method is a difficult technical problem. Furthermore, generally the foaming product obtained does not show sufficient stability.

[0005]

[Means for Solving the Problem] The object of this invention is offer of the foaming product of the good mechanical property which does not show the fault which influences a conventional method, and the biodegradability plastic material which has good elasticity and compressibility especially. Therefore, the object of this invention 0.1 - 0.003 g/cm³ The consistency of the range, and diameter It is the foaming product made from biodegradability plastic material which are consisted of by the condensation foaming particle which has the magnitude of the range of 0.5-10mm, and a particle consists of with the following ingredient.

[0006] - thermoplastic starch 50 - 95wt% -- desirable -- 60 - 95wt% and at least one thermoplastic polymer 0.5 - 45wt% -- desirable -- 2-35wt% and water 2 - 20wt% -- desirable -- the foaming particle which constitutes the foaming product of 5-17wt% this invention -- desirable -- 0.06 - 0.005 g/cm³ the consistency of the range -- and -- desirable -- It has the magnitude of the range of one to 5 mm.

[0007] Said foaming particle has closed cell structure. They can have various configurations, especially the configuration of a parenchyma top ball. One or the existence of the thermoplastic polymer beyond it in the constituent of the above-mentioned foaming particle enables amelioration of the melt strength of a constituent, and can give good elasticity and low moisture-sensitive nature with a foaming product.

[0008] the thermoplastic starch which can be used as a component of said foaming particle --

natural starch -- they are corn starch, potato starch or a high amylose starch grade, the thing that contains an amylose 30% or more preferably, and a wax starch grade preferably. Furthermore, the ethoxy rate starch which has the substitutional rate of the range of 0.1 as starch by which refining was carried out physically and chemically, Oxy-PUROI rate starch, acetate starch, butyrate starch, propionate starch; Cation starch, Oxidized starch, bridge formation starch, gelation starch, and the polymer that can give "V"-type complex, For example, starch compounded by ethylene-vinyl alcohol (EVOH), the ethylene-acrylic acid (EAA), the ERECHIN-maleic-anhydride copolymer, and the ethylene-ethyl acrylate-maleic-anhydride terpolymer; graft-ized starch, decomposition starch, and destructive starch can be used.

[0009] Natural starch is abbreviation. It is used including 9 - 16wt% water, without usually presenting preliminary dehydration. The thermoplastic polymer which can be used for the constituent of a foaming particle is chosen from a degree.

i. Cellulose acetate or cellulose butyrate which has the substitutional rate of the range of 1-2.5, and may be plasticized, Alkyl cellulose, a hydroxyalkyl cellulose, carboxy alkyl cellulose, Unimproving [a natural polymer like especially methyl cellulose, amelioration, or], especially -- a cellulosic -- and -- further -- chitosan, a shellac or casein, and caseinate -- ii. The biodegradability polymer obtained by composition or fermentation, especially polyester, For example, the gay and copolymer of aliphatic series C2-C24 hydroxy acid, its corresponding lactone, or a lactide, And the polyester further guided from the acid and aliphatic series dialcohol of two functional values, For example, - Pori (EPISHIRON-caprolactone), its graft, or a block copolymer, Caprolactone oligomer or a polymer, aromatic series, or a resultant with aliphatic series isocyanate, - The polymer of a lactic acid or the polymer of a lactide, a glycolic acid, or poly glycolide, The copolymer of a lactic acid and a glycolic acid, polyhydroxy butyrate, or polyhydroxy butyrate-valerate, - polyalkylene succinate -- and -- especially -- polyethylene succinate or polybutylene succinate -- A polyethylene horse mackerel peat or a polybutylene horse mackerel peat, polyethylene sebacate, or polybutylene sebacate, polyethylene azelate or polybutylene azelate, a polyethylene brush rate or polybutylene brush rates, and those copolymers (-izing can be carried out [copolymerization] with aliphatic series or aromatic series isocyanate --) Furthermore, these are good iii. amyloses, even if it increases molecular weight by the chain extension agent. The polymer which "V"-type complex can form, or the polymer containing the hydrophilic group which intervened the hydrophobic array, for example, an ethylene unit, -- up to 50wt(s)% -- desirable -- 10 - 44wt% -- the included ethylene-vinyl alcohol polymer -- With the ethylene-vinyl alcohol copolymer which oxidized, or a fatty acid, terminalization, By the poly caprolactone, by the acrylic and/or pyridinium of graft-izing or an methacrylic monomer Or the ethylene-vinyl alcohol copolymer of refining, - The ethylene-vinyl acetate copolymer which may be hydrolyzed selectively, - An ethylene-acrylic ester copolymer, ethylene-acrylic An ester-maleic anhydride or ethylene-vinyl acetate-glycidyl The terpolymer of a meta-crate, - An ethylene copolymer with an acrylic acid, a methacrylic acid, a crotonic acid, an itaconic acid, and a partial saturation acid like a maleic anhydride, unit guided [especially] from an acrylic acid 5-50-mol % -- desirable -- 10-30-mol % -- with the included ethylene-acrylic-acid copolymer and the vinyl acetate which may be hydrolyzed on the whole or selectively An ethylene terpolymer with an acrylic acid, a methacrylic acid, a crotonic acid, or an itaconic acid, - Aliphatic series 6-6, 6-9 or 12 polyamides, aliphatic series polyurethane, Random or a block polyurethane-polyamide, polyurethane-polyester, A polyurethane-polyether, polyamide-polyester, a polyamide-polyether, A polyester-polyether copolymer and iv. The polymer which can form starch and hydrogen bond, Pori by which refining may be especially carried out by acrylate or methacrylate at the various rates of hydrolysis (vinyl alcohol), Were improved in order to reduce plasticization or those melting points beforehand. Or Pori which may also contain boric acid, borate, and a gelling agent like phosphate (vinyl alcohol); vinyl pyrrolidone or a vinyl acetate copolymer (various rates of hydrolysis) with styrene, poly ethyl oxazoline, polyvinyl pyridine.

[0010] Desirable thermoplastic polymers are the copolymer of Pori (vinyl alcohol), an olefin monomer, and an ethylene and the monomer chosen from vinyl alcohol, vinyl acetate, an acrylic acid, and a methacrylic acid, the poly caprolactone, Pori (BUCHIRUREN succinate), aliphatic series polyester like those copolymers, and an aliphatic series polyamide preferably.

[0011] The foaming particle which constitutes the foaming product of this invention contains a nucleating additive preferably. the amount of such a nucleating additive in the charge of foam,

and 0.005 - 5wt% -- desirable -- 0.05 - 3wt% -- more -- desirable -- It consists of the range of 0.2 - 2wt%. The nucleating additives which can be used are silanes, such as talc (magnesium silicate) and a calcium carbonate or titanate in an inorganic compound. [0012] Furthermore, organic bulking agents, such as the yeast shell (yeast shells) of sugarbeet processing, desiccation, grinding and a mesophyll of the sugarbeet which carried out disintegration, wood flour, and cellulose powder, can be used. A nucleating additive can be added to the mixture which makes a foaming particle, or can be instead added to the foaming particle as a masterbatch. In the case of the latter, a masterbatch can include one or the bulking agent beyond it 10 to 50%.

[0013] furthermore, a foaming particle -- the slipping agent beyond one or it -- and/or -- the range of 3-25 -- desirable -- A dispersant with the hydrophilic property / oleophilic balance characteristic of the range of 6-20 (HLB) can be included. the time of using it -- these additives -- 0.01 - 5wt% -- the amount of the range of 0.1 - 3wt% can be given preferably. A foaming particle can also include one or the plasticizer beyond it. the time of using it -- said plasticizer and 0.5 - 20wt% -- desirable -- The amount of the range of 0.5 - 5.0wt% can be given.

[0014] The plasticizer which can be used is *****. It is indicated by WO 92/No. 14,782, and the content is introduced here. what is suitable for an activity especially as a plasticizer -- a glycol, a sorbitol, a mannitol, an erythritol, low-molecular-weight Pori (vinyl alcohol), those oxy-ethylates, and an oxy-PUROPI rate derivative -- and it is a urea further.

[0015] Furthermore, a foaming particle can include one or the flame retarder beyond it, and can add it to the mixture which makes a foaming particle, or, instead, can be added to the foaming particle as a masterbatch especially combining a nucleating additive. the time of using them -- said flame retarder 0.1 - 20wt% -- desirable -- 1 - 10wt% -- more -- desirable -- The amount of the range of 2 - 5wt% is given.

[0016] A flame retarder is chosen from the compound led from the Lynn inclusion, a sulfur inclusion, or a halogenated compound. for example, triphenyl phosphate, tributyl phosphate, tricresyl phosphate, TORIBUTOKISHI phenyl phosphate, melamine pyrophosphate, ammonium poly phosphate, ethylenediamine, guanidinium phosphate, a tetrabromophthalic anhydride, halogenation paraffin, and bromination -- the diphenyloxide from which a rate differs, ammonium sulfate, an ammonium SURUFA mate, etc. are suitable for the desired object. Ammonium sulfate, an ammonium SURUFA mate, ammonium poly phosphate, guanidinium phosphate, and especially melamine pyrophosphate are advantageous.

[0017] The flame retarders which can use others are an aluminum hydroxide, an antimony trioxide, perboric acid ammonium, an ammonium OKUTAMO rib date, etc. When existence of the repellent to a rodent is required, they can be added to the mixture which makes a foaming particle, or can be added to a foaming particle as a masterbatch especially as an active substance content microcapsule about a special application side combining a nucleating additive and/or a flame retarder.

[0018] An N and N-diethyl-m-torr amide, diethyl phenyl acetamido, a 2-decanal ** ammonium chloride, potassium chlorate, terpenoid, a cycloheximide, jig ANIJINO aza-heptadecane, etc. can be used for this object. terpenoid -- and [especially] menthol and a limonene are desirable. the time of an activity -- those repellent and 0.1 - 5wt% -- desirable -- The amount of the range of 1 - 3wt% is given.

[0019] The foaming particle which constitutes the foaming product of this invention can be manufactured by the approach of the extrusion of a starch system constituent, and a monopodium or a twin screw extruder can perform it. Such an extrusion process It carries out under existence of the water of the amount of the range of 5 - 20wt%, and the starch contained in a constituent is destroyed. However, the content of water should be controlled by the ventilator style to be the range whose total moisture content in a nozzle is 5 - 20wt%.

[0020] Instead, granulation can use the granulation of the thermoplastic starch beforehand destroyed by the well-known approach. For example, ***** WO92 / No. 02 or 363, and ** WO92 / the content of No. 14 or 728 is introduced into this description. Generally the aforementioned extrusion process is. It is the temperature of the range of 150 to 250 degree C, and, generally is carried out by the residence time for 15 minutes from 20 seconds. Noodle cutting (pelletizing) of an extrusion head lower stream of a river is performed at high speed, while the melting ingredient is not solidifying, it is cut, and the obtained particle (pellet) turns into an

almost spherical particle. Generally, the shearing value of an extrusion head is higher than 1000s-1, and higher than 3000s-1.

[0021] The another manufacture approach of a foaming particle consists of processing of compression/reduced pressure of a non-foamed particle with the magnitude of the range of 20 micrometers - 1 mm particle size. The aforementioned non-foamed particle can be extruded with a multi-aperture die, and, subsequently can be obtained by grinding of the granulation of head cutting or a large dimension. At the temperature of the range of 40 to 200 degree C, under existence of moisture [**** / water / which is contained in an ingredient], these non-foamed particles are given to the pressure of the range of 2-100 bars, and, subsequently rapid reduced pressure is presented with them.

[0022] The manufacture approach of a foaming particle another again consists of presenting heat treatment by microwave with the aforementioned non-foamed particle. The foaming product made from biodegradability plastic material of this invention can be manufactured according to the condensation process of the foaming particle of said ingredient: thermoplastic starch 50 - 95wt% -- desirable -- 60 - 95wt% and at least one thermoplastic polymer 0.5 - 45wt% -- desirable -- With the ingredient which consists of 2 - 35wt% water 2 - 20wt% -- desirable -- it consists of 5 - 17wt% -- 0.1 - 0.005 g/cm3 Consistency of the range The foaming particle of the magnitude of the range of 0.5-10mm diameter In order to reform the front face of the particle so that an interaction may be carried out stably mutually when carrying out mutual homogeneity contact of these, it is given to heat treatment and/or processing with at least one coating. Subsequently It is the manufacturing method of the foaming product made from sufficient long time amount for making the foaming particle condense, and the biodegradability plastic material which consists of holding homogeneity contact mutually.

[0023] The good resilience property of a foaming particle can be borne at any colla tempestade PUSHINGU (cellular destruction) phenomena, when a particle is in homogeneity contact. Coating which can be used by the approach by this invention For example, i. Water of the liquid which may add a salt and/or an additive, or gaseous water, ii. The solution, the water suspension, or the water emulsion of nature or composition, a giant molecule, or the matter of a monomer, or said matter by the melting condition and iii. -- a solvent with wetting power high enough, and iv. Nature or composition in said solvent, a giant molecule or the solution of the matter of a monomer, suspension or an emulsion, and v. The melting point 130 degrees C or less -- desirable -- polymer 90 degrees C or less.

[0024] The example of coating which can be used for a solution, suspension, or an emulsion water by the approach of this invention - Pori (vinyl acetate), - Pori (vinyl butyrate), vinyl acetate, or vinyl butyrate and vinyl ester, By the copolymer with the monomer beyond one or it chosen from acrylate, methacrylate, an allyl compound derivative, pyridinium salt, acrylonitrile, acrylamide, vinyl pyrrolidone, vinylpyridine, and vinyl imidazole Aliphatic series polyester [like - poly caprolactone by which a part or all may be hydrolyzed] these [whose] are or a lactic-acid polymer, graft-ized Pori (vinyl acetate), or Pori (vinyl butyrate), - Pori as for which refining was carried out by Pori (vinyl alcohol) which may mix conditioning with a plasticizer and/or boric acid, borate, and a gelling agent like titanate, - acetalization, etherification, or esterification at high or the rate of low hydrolysis (vinyl alcohol)

- The block copolymer of Pori (vinyl alcohol) with Pori (vinyl acetate or styrene), - Pori (vinyl alcohol) of a fatty-acid cap, a polyoxyethylene and/or polyoxypropylene, and graft-ized Pori (vinyl alcohol), - Oxidation the natural starch of all the origins, hydroxyalkyl-izing, and cationicity -- The starch by which refining was carried out by the starch constructed [the bridge] for which and hydrolyzed or ester, the ether, and/or the phosphoric-acid radical, - Casein and caseinate, alkyl cellulose, a hydroxyalkyl cellulose, and cellulose ester, For example, the cellulose acetate and the carboxymethyl cellulose by which refining may be carried out with plasticization and/or aliphatic series ester like a caprolactone, - Natural rubber like natural rubber latex, - acrylamide, acrylonitrile, styrene or acrylic ester, and the gum Arabic that may be graft-ized (vegetable hydrocolloid), - An alginic acid, alginate, an abietic acid, rosin resin, an agar, GUYAGAMU, KARAGININ, xanthene rubber, a pullulan, chitosan, a shellac, animal gelatin, A protein, an emulsifier, a dispersant, a bulking agent, - Pori (acrylic acid), ethylene / acrylic-acid copolymer, Ammonium or sodium salt of acrylamide / acrylic-acid copolymer, and the ionicity polymer guided from Pori (styrene sulfonic acid), Generally - The gay and copolymer, especially the poly

caprolactone of a property of aliphatic series, Those copolymers with polyurethane like Pori (lactic acid), Pori (hydroxy butyrate BARETO), and Pori (butanediol succinate), a polyamide, polyester, and the polyfunctional alcohol are added selectively.

[0025] In the matter mentioned above, especially Pori (vinyl acetate) is suitable for the activity as coating by the approach by this invention. As for the manufacturing method of the foaming product of this invention, it is desirable to continue simultaneous before a homogeneity contact **** process, and to consist a particle of heat and/or a process which carries out aeration processing because of acceleration of polymerization-izing of the monomer matter contained in evaporation and/or coating of the liquefied matter.

[0026] It is suitable to present back desiccation processing with the foaming product obtained further. After this, desiccation processing can make the water or the solvent which remains able to remove, and can be performed under desiccation, humidity, or the conditions that were adjusted. a polymer -- in the case of coating which consists of a monomer [-izing / a monomer], a polymerization reaction and/or particle condensation can use said after treatment for a completion **** sake. Furthermore, said back desiccation processing phase can stabilize the configuration of the product obtained.

[0027] the case where coating is used with an emulsion gestalt -- the range of 0.05 - 3wt% -- desirable -- the range of 0.1 - 2wt% -- more -- desirable -- An emulsifier and/or a thickener can be included in the amount of the range of 0.2 - 1wt%. the emulsifier which can be used -- for example, -- 3-25 -- desirable -- It is a surfactant with the hydrophilic property / oleophilic balance characteristic of the range of 6-20 (HLB). what esterified the polyoxyethylene (4-20 mols) which esterified a polyoxyethylene or polyoxypropylene in the effective surface active agent especially with what was directly esterified with the fatty acid, for example, a lauric acid, a palmitic acid, or stearin acid, or polyoxyethylene-ized sugar with the fatty acid -- for example, -- the oxy-ethylation (4-20 mols) sorbitol esterified with the 1-6-mol fatty acid, and ** -- there is a thing of induction from a polyoxyethylene or polyoxypropylene. [like] Furthermore, the surface active agents which can be used are the polyoxyethylene ether with oxy-ethylation nonyl phenol, the lanolin ether and ester, tree ethanolamine oleate and the poly glycerol ester of a fatty acid, for example, stearyl alcohol, cetyl alcohol, or fatty alcohol like cholesterol, a PEG-beef tallow amide, and PEG-castor oil.

[0028] The thickeners which can be used are carboxymethylcellulose sodium, methyl cellulose, natural rubber, clay, etc. According to the desirable mode, the approach of this invention can be suitably performed by using the format of equipment as shown in drawing 1 . In drawing 1 , the citation numbers 1, 3, and 9 operate by the compressed air respectively by the closing motion system which shows the separation wall which can be slid and is shown by 2, 4, and 10.

[0029] The separation wall 1 is opened and a measuring chamber 5 is filled up with a foaming particle. Subsequently, the separation wall 1 is shut, the separation wall 3 is opened, and a particle is entrapped to an atomizing chamber 6. subsequently, enough to shut the separation wall 3, start actuation of the sprayer 7 containing coating, and saturate an atomizing chamber 6 with coating -- long -- time amount actuation is carried out. A sprayer 7 is stopped here, the separation wall 9 is opened, and a particle is entrapped into a duct 11. The parts 14 and 15 of a mould which are a male and a female respectively are held in such a location. The width of face of the air spacing 16 in the meantime is smaller than the diameter of a pellet. The separation wall 9 is shut, a particle is supplied to a mould side with a piston 12, and a pressure is put on them. Finally a mould is opened with a piston 17 and the products obtained are collected.

[0030] According to another desirable mode, the approach of this invention can be suitably performed by giving a supply path to the molding room of the same equipment (mould with aeration puncturing) with having used for sintering a form polystyrene particle, and giving a **** and a foaming particle to processing with coating directly. Finally, coating can supply a foaming particle suitably directly through the hole of a mould after filling up a mould.

[0031] The following example is not given for the purpose of instantiation, and does not limit this invention.

The trial of characterization resilience ***** measures the ingredient engine performance recovered to the initial form, after adding the load which brings about deformation.

[0032] Diameter 125mm and height A 150mm cylinder container is filled up with a foaming particle, the flat sensor of a load cell is pushed in, and it is made to operate the rate for 25mm/. A

sensor pushes a particle in 33% of cylinder height, and, subsequently to a start location, returns a sensor. A sensor performs 2nd particle compression actuation by the same actuation as the 1st time after 1 minute. The resilience value reported for a% of numeric value is 100 times the ratio which broke the load of the 1st compression actuation by the load of the 2nd compression actuation.

Consistency Dapp (kg/m³) The ** (appearance) consistency of the foaming particle computed from the weight of 5l. of particles, and Dbulk (kg/m³) The specific gravity consistency of each foaming particle, and Dexp (kg/m³) Specific gravity consistency of a foaming product.

[0033]

[Example]

Example 1 mixture was made from the following constituents.

– potato starch Pori (vinyl alcohol) 10wt% and water of 75wt% and 86% of rates of hydrolysis 15 – wt % -- this -- a constituent -- a diameter -- (– d –) -- 30 -- mm -- die length -- a diameter -- a ratio -- [– (– L –) – /– (– d –) –] -- 30 -- a twin screw extruder -- APV2030 was supplied. The operating condition was performed as follows.

[0034] – Screw rotational speed 150rpm and temperature gradient 69 degree-C/100 degree-C/180 degree-C/170 degree-C/155 degree C and extrusion outlet It adjusted so that 10kg [/] all moisture content might be held to about 14% an hour. the obtained pellet -- mean-particle-diameter abbreviation 1.5 micrometers Talc 0.5 -- % -- a diameter -- (– d –) -- 40 -- mm – [– (– L –) – /– (– d –) –] -- 28 -- a monopodium -- a screw extruder -- ex OMC supplying -- diameter (d) 0.8 mm and [(L)/(d)] It equipped with the extrusion head of one or less nozzles [four].

[0035] The operating condition was performed as follows.

– Screw rotational speed 40rpm and temperature gradient 80 degree-C/120 degree-C/190 degree-C/190 degree-C/200 degree C and extrusion outlet 52kg/hour and head cutting cutting-edge rotational speed The pellet of the charge of 4000rpm foam was obtained. A property is shown in a table 1.

[0036]

[A table 1]

An example Particle size Dapp Dbulk Resilience (mm) (kg/m³) (kg/m³) (%) 1 3.5 15 32 65 2 3.0 10 21 71 3 3.2 14 2875 4 3.3 21 39 65 5 3.2 16 35 68 6 3.5 21 40 58 example 2 operating instructions presupposed that it is the same as that of an example 1, and used the mixture of the following constituents.

[0037] – potato starch 64wt% and 99.8% of rates of hydrolysis, molecular weight (Mw) 70,000, and an ethylene unit -- 44-mol % -- included EVOH 25wt% and water 10wt% – glycerol mono-olate 1wt% -- the moisture content in a pellet was about 10%. The property of a foaming pellet is shown in a table 1.

Example 3 operating instructions presupposed that it is the same as that of an example 1, and used the mixture of the following constituents.

[0038] – potato starch 78wt% and 99.8% of rates of hydrolysis, molecular weight 70,000, and an ethylene unit -- 44-mol % -- Pori (vinyl alcohol) of EVOH 7wt% and 86% of included rates of hydrolysis 8wt% and water 6wt% – glycerol mono-olate 1wt% -- the moisture content in a pellet was about 12%. The property of a foaming pellet is shown in a table 1.

Example 4 operating instructions presupposed that it is the same as that of an example 1, and used the mixture of the following constituents.

[0039] – potato starch 68wt% and poly caprolactone (UC PCL 787) 10wt%, caprolactone-urethane block-copolymer (Pellethane 2102-85AE9) 5wt%, and water 15wt% – glycerol mono-olate 1wt% -- the moisture content in a pellet was about 10%. The property of a foaming pellet is shown in a table 1.

Example 5 operating instructions presupposed that it is the same as that of an example 1, and used the mixture of the following constituents.

[0040] – potato starch Ethylene-acrylic-acid copolymer (Dow Chemical Co. make) which includes 75wt% and an acrylic unit for 20-mol % 10wt% and water 15wt% -- the moisture content in a pellet was about 10%. The property of a foaming pellet is shown in a table 1.

Example 6 operating instructions presupposed that it is the same as that of an example 1, and used the mixture of the following constituents.

[0041] - potato starch Substitutional rate plasticized at 75wt% and caprolactone 20% Cellulose acetate of 2.5 10wt% and water 15wt% -- the moisture content in a pellet was about 12%. The property of a foaming pellet is shown in a table 1.

The measuring chamber 5 of the equipment shown in example 7 drawing 1, capacity The foaming particle obtained by 2l. in the example 3 was supplied.

[0042] Subsequently, it processed by the VINABIRU (Vinavil) NPC emulsion (Enichem Systhesis) which contains Pori (vinyl acetate) 50% by the above-mentioned approach, and atomized with the sprayer 7. Back desiccation processing was performed to the reaction chamber which controlled the obtained manufacture to 23 degrees C and (relative humidity RH) 30% for 15 hours.

[0043] The property of a foaming product is shown in a table 2.

[0044]

[A table 2]

An example Mould temperature Dexp Longitudinal shrinkage (degree C) (kg/m3) (%) 7 20 50 3 8

20 43 3.5 9 20 40 4 10 20 36 511 20 25 1 12 20 60 23 13 30 4612 Example 8 operating instructions presupposed that it is the same as that of an example 7. At this time, it is dilution with the water of a VINABIRU (Vinavil) NPC emulsion (Enichem Systhesis). It could be 1/10 (water/Vinavil).

[0045] The property of a foaming product is shown in a table 2.

Example 9 operating instructions presupposed that it is the same as that of an example 7. At this time, it is dilution with the water of a VINABIRU (Vinavil) NPC emulsion (Enichem Systhesis). It was referred to as 1/5 (water/Vinavil).

[0046] The property of a foaming product is shown in a table 2.

Example 10 operating instructions presupposed that it is the same as that of an example 7. At this time, it is dilution with the water of a VINABIRU (Vinavil) NPC emulsion (Enichem Systhesis). It was referred to as 1/2 (water/Vinavil).

[0047] The property of a foaming product is shown in a table 2.

Example 11 operating instructions presupposed that it is the same as that of an example 10, and a different point used what was obtained from the example 2 for the foaming pellet. The property of a foaming product is shown in a table 2.

Example 12 operating instructions presupposed that it is the same as that of an example 10, and a different point used what was obtained from the example 1 for the foaming pellet.

[0048] The property of a foaming product is shown in a table 2.

Example 13 operating instructions presupposed that it is the same as that of an example 10, and a different point performed back desiccation processing in 23 degrees C and the reaction chamber controlled to RH55% for 15 hours. The property of a foaming product is shown in a table 2.

[0049]

[Effect of the Invention] According to this invention, a good mechanical property, the foaming product made from biodegradability plastic material with especially good elasticity and compressibility, and its manufacture approach are offered.

[Translation done.]

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TECHNICAL FIELD

[Industrial Application] This invention relates to the foaming product made from biodegradability plastic material, and its manufacturing method.

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PRIOR ART

[Description of the Prior Art] In the field of the invention of the charge of foam especially used for a protective package, the need for the ingredient which satisfies the requirements for stronger biodegradability as an alternative of form polystyrene is searched for. The activity of a **** system ingredient was conventionally proposed by this object.

[0003] European Patent ** No. A-0,087,847 heats the base material containing starch or starch with extrusion pressure under existence of water 10 - 30wt% and a foaming agent, subsequently extrudes it, and is indicating the manufacturing method of a starch system foaming product.

European Patent ** No. A-0,375,831 is indicating the good foaming product which consists of mechanical and high amylose starch showing a closed cell structure property. These foaming products are extruded at the temperature of the bottom of existence of water, and the range of 150 to 250 degree C, probably carry out thermoforming processing, and are manufactured.

[0004] the [international patent application] -- WO 91 / No. 02 or 023 are indicating the foaming product of the biodegradability plastic material which carries out extrusion molding of the synthetic macromolecule chosen from the constituent containing starch, ethylene, vinyl alcohol, and an ethylene-acrylic-acid copolymer under existence of the sodium hydrogencarbonate as polyacid and a foaming agent. However, manufacture of the foaming product which has a complicated configuration or thickness in actuation by the conventional method is a difficult technical problem. Furthermore, generally the foaming product obtained does not show sufficient stability.

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EFFECT OF THE INVENTION

[Effect of the Invention] According to this invention, a good mechanical property, the foaming product made from biodegradability plastic material with especially good elasticity and compressibility, and its manufacture approach are offered.

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MEANS

[Means for Solving the Problem] The object of this invention is offer of the foaming product of the good mechanical property which does not show the fault which influences a conventional method, and the biodegradability plastic material which has good elasticity and compressibility especially. Therefore, the object of this invention 0.1 - 0.003 g/cm³ The consistency of the range, and diameter It is the foaming product made from biodegradability plastic material which are consisted of by the condensation foaming particle which has the magnitude of the range of 0.5-10mm, and a particle consists of with the following ingredient.

[0006] - thermoplastic starch 50 - 95wt% -- desirable -- 60 - 95wt% and at least one thermoplastic polymer 0.5 - 45wt% -- desirable -- 2-35wt% and water 2 - 20wt% -- desirable -- the foaming particle which constitutes the foaming product of 5-17wt% this invention -- desirable -- 0.06 - 0.005 g/cm³ the consistency of the range -- and -- desirable -- It has the magnitude of the range of one to 5 mm.

[0007] Said foaming particle has closed cell structure. They can have various configurations, especially the configuration of a parenchyma top ball. One or the existence of the thermoplastic polymer beyond it in the constituent of the above-mentioned foaming particle enables amelioration of the melt strength of a constituent, and can give good elasticity and low moisture-sensitive nature with a foaming product.

[0008] the thermoplastic starch which can be used as a component of said foaming particle -- natural starch -- they are corn starch, potato starch or a high amylose starch grade, the thing that contains an amylose 30% or more preferably, and a wax starch grade preferably. Furthermore, the ethoxy rate starch which has the substitutional rate of the range of 0.1-2 as starch by which refining was carried out physically and chemically, Oxy-PUROI rate starch, acetate starch, butyrate starch, propionate starch; Cation starch, Oxidized starch, bridge formation starch, gelation starch, and the polymer that can give "V"-type complex, For example, starch compounded by ethylene-vinyl alcohol (EVOH), the ethylene-acrylic acid (EAA), the ERECHIN-maleic-anhydride copolymer, and the ethylene-ethyl acrylate-maleic-anhydride terpolymer; graft-ized starch, decomposition starch, and destructive starch can be used.

[0009] Natural starch is abbreviation. It is used including 9 - 16wt% water, without usually presenting preliminary dehydration. The thermoplastic polymer which can be used for the constituent of a foaming particle is chosen from a degree.

i. Cellulose acetate or cellulose butyrate which has the substitutional rate of the range of 1-2.5, and may be plasticized, Alkyl cellulose, a hydroxyalkyl cellulose, carboxy alkyl cellulose, Un-improving [a natural polymer like especially methyl cellulose, amelioration, or], especially -- a cellulosic -- and -- further -- chitosan, a shellac or casein, and caseinate -- ii. The biodegradability polymer obtained by composition or fermentation, especially polyester, For example, the gay and copolymer of aliphatic series C₂-C₂₄ hydroxy acid, its corresponding lactone, or a lactide, And the polyester further guided from the acid and aliphatic series dialcohol of two functional values, For example, - Pori (EPISHIRON-caprolactone), its graft, or a block copolymer, Caprolactone oligomer or a polymer, aromatic series, or a resultant with aliphatic series isocyanate, - The polymer of a lactic acid or the polymer of a lactide, a glycolic acid, or poly glycolide, The copolymer of a lactic acid and a glycolic acid, polyhydroxy butyrate, or polyhydroxy butyrate-valerate, - polyalkylene succinate -- and -- especially -- polyethylene succinate or polybutylene succinate -- A polyethylene horse mackerel peat or a polybutylene

horse mackerel peat, polyethylene sebacate, or polybutylene sebacate, polyethylene azelate or polybutylene azelate, a polyethylene brush rate or polybutylene brush rates, and those copolymers (—izing can be carried out [copolymerization] with aliphatic series or aromatic series isocyanate —) Furthermore, these are good iii. amyloses, even if it increases molecular weight by the chain extension agent. The polymer which "V"-type complex can form, or the polymer containing the hydrophilic group which intervened the hydrophobic array, for example, an ethylene unit, — up to 50wt(s)% — desirable — 10 – 44wt% — the included ethylene-vinyl alcohol polymer — With the ethylene-vinyl alcohol copolymer which oxidized, or a fatty acid, terminalization, By the poly caprolactone, by the acrylic and/or pyridinium of graft-izing or an methacrylic monomer Or the ethylene-vinyl alcohol copolymer of refining, – The ethylene-vinyl acetate copolymer which may be hydrolyzed selectively, – An ethylene-acrylic ester copolymer, ethylene-acrylic An ester-maleic anhydride or ethylene-vinyl acetate-glycidyl The terpolymer of a meta-crate, – An ethylene copolymer with an acrylic acid, a methacrylic acid, a crotonic acid, an itaconic acid, and a partial saturation acid like a maleic anhydride, unit guided [especially] from an acrylic acid 5–50–mol % — desirable — 10–30–mol % — with the included ethylene-acrylic-acid copolymer and the vinyl acetate which may be hydrolyzed on the whole or selectively An ethylene terpolymer with an acrylic acid, a methacrylic acid, a crotonic acid, or an itaconic acid, – Aliphatic series 6–6, 6–9 or 12 polyamides, aliphatic series polyurethane, Random or a block polyurethane-polyamide, polyurethane-polyester, A polyurethane-polyether, polyamide-polyester, a polyamide-polyether, A polyester-polyether copolymer and iv. The polymer which can form starch and hydrogen bond, Pori by which refining may be especially carried out by acrylate or methacrylate at the various rates of hydrolysis (vinyl alcohol), Were improved in order to reduce plastic<DP N==0004>-izing or those melting points beforehand. Or Pori which may also contain boric acid, borate, and a gelling agent like phosphate (vinyl alcohol); vinyl pyrrolidone or a vinyl acetate copolymer (various rates of hydrolysis) with styrene, poly ethyl oxazoline, polyvinyl pyridine.

[0010] Desirable thermoplastic polymers are the copolymer of Pori (vinyl alcohol), an olefin monomer, and an ethylene and the monomer chosen from vinyl alcohol, vinyl acetate, an acrylic acid, and a methacrylic acid, the poly caprolactone, Pori (BUCHIRUREN succinate), aliphatic series polyester like those copolymers, and an aliphatic series polyamide preferably.

[0011] The foaming particle which constitutes the foaming product of this invention contains a nucleating additive preferably. the amount of such a nucleating additive in the charge of foam, and 0.005 – 5wt% — desirable — 0.05 – 3wt% — more — desirable — It consists of the range of 0.2 – 2wt%. The nucleating additives which can be used are silanes, such as talc (magnesium silicate) and a calcium carbonate, or titanate in an inorganic compound.

[0012] Furthermore, organic bulking agents, such as the yeast shell (yeast shells) of sugarbeet processing, desiccation, grinding and a mesophyll of the sugarbeet which carried out disintegration, wood flour, and cellulose powder, can be used. A nucleating additive can be added to the mixture which makes a foaming particle, or can be instead added to the foaming particle as a masterbatch. In the case of the latter, a masterbatch can include one or the bulking agent beyond it 10 to 50%.

[0013] furthermore, a foaming particle — the slipping agent beyond one or it — and/or — the range of 3–25 — desirable — A dispersant with the hydrophilic property / oleophilic balance characteristic of the range of 6–20 (HLB) can be included. the time of using it — these additives — 0.01 – 5wt% — the amount of the range of 0.1 – 3wt% can be given preferably. A foaming particle can also include one or the plasticizer beyond it. the time of using it — said plasticizer and 0.5 – 20wt% — desirable — The amount of the range of 0.5 – 5.0wt% can be given.

[0014] The plasticizer which can be used is *****. It is indicated by WO 92/No. 14,782, and the content is introduced here. what is suitable for an activity especially as a plasticizer — a glycol, a sorbitol, a mannitol, an erythritol, low-molecular-weight Pori (vinyl alcohol), those oxy-ethylates, and an oxy-PUROPI rate derivative — and it is a urea further.

[0015] Furthermore, a foaming particle can include one or the flame retarder beyond it, and can add it to the mixture which makes a foaming particle, or, instead, can be added to the foaming particle as a masterbatch especially combining a nucleating additive. the time of using them — said flame retarder 0.1 – 20wt% — desirable — 1 – 10wt% — more — desirable — The amount of the range of 2 – 5wt% is given.

[0016] A flame retarder is chosen from the compound led from the Lynn inclusion, a sulfur

inclusion, or a halogenated compound. for example, triphenyl phosphate, tributyl phosphate, tricresyl phosphate, TORIBUTOKISHI phenyl phosphate, melamine pyrophosphate, ammonium poly phosphate, ethylenediamine, guanidinium phosphate, a tetrabromophthalic anhydride, halogenation paraffin, and bromination -- the diphenyloxide from which a rate differs, ammonium sulfate, an ammonium SURUFA mate, etc. are suitable for the desired object. Ammonium sulfate, an ammonium SURUFA mate, ammonium poly phosphate, guanidinium phosphate, and especially melamine pyrophosphate are advantageous.

[0017] The flame retarders which can use others are an aluminum hydroxide, an antimony trioxide, perboric acid ammonium, an ammonium OKUTAMO rib date, etc. When existence of the repellent to a rodent is required, they can be added to the mixture which makes a foaming particle, or can be added to a foaming particle as a masterbatch especially as an active substance content microcapsule about a special application side combining a nucleating additive and/or a flame retarder.

[0018] An N and N-diethyl-m-torr amide, diethyl phenyl acetamido, a 2-decanal ** ammonium chloride, potassium chlorate, terpenoid, a cycloheximide, jig ANIJINO aza-heptadecane, etc. can be used for this object. terpenoid -- and [especially] menthol and a limonene are desirable. the time of an activity -- those repellent and 0.1 - 5wt% -- desirable -- The amount of the range of 1 - 3wt% is given.

[0019] The foaming particle which constitutes the foaming product of this invention can be manufactured by the approach of the extrusion of a starch system constituent, and a monopodium or a twin screw extruder can perform it. Such an extrusion process It carries out under existence of the water of the amount of the range of 5 - 20wt%, and the starch contained in a constituent is destroyed. However, the content of water should be controlled by the ventilator style to be the range whose total moisture content in a nozzle is 5 - 20wt%.

[0020] Instead, granulation can use the granulation of the thermoplastic starch beforehand destroyed by the well-known approach. For example, ***** WO92 / No. 02 or 363, and ** WO92 / the content of No. 14 or 728 is introduced into this description. Generally the aforementioned extrusion process is. It is the temperature of the range of 150 to 250 degree C, and, generally is carried out by the residence time for 15 minutes from 20 seconds. Noodle cutting (pelletizing) of an extrusion head lower stream of a river is performed at high speed, while the melting ingredient is not solidifying, it is cut, and the obtained particle (pellet) turns into an almost spherical particle. Generally, the shearing value of an extrusion head is higher than 1000s-1, and higher than 3000s-1.

[0021] The another manufacture approach of a foaming particle consists of processing of compression/reduced pressure of a non-foamed particle with the magnitude of the range of 20 micrometers - 1 mm particle size. The aforementioned non-foamed particle can be extruded with a multi-aperture die, and, subsequently can be obtained by grinding of the granulation of head cutting or a large dimension. At the temperature of the range of 40 to 200 degree C, under existence of moisture [**** / water / which is contained in an ingredient], these non-foamed particles are given to the pressure of the range of 2-100 bars, and, subsequently rapid reduced pressure is presented with them.

[0022] The manufacture approach of a foaming particle another again consists of presenting heat treatment by microwave with the aforementioned non-foamed particle. The foaming product made from biodegradability plastic material of this invention can be manufactured according to the condensation process of the foaming particle of said ingredient. thermoplastic starch 50 - 95wt% -- desirable -- 60 - 95wt% and at least one thermoplastic polymer 0.5 - 45wt% -- desirable -- With the ingredient which consists of 2 - 35wt% water 2 - 20wt% -- desirable -- it consists of 5 - 17wt% -- 0.1 - 0.005 g/cm3 Consistency of the range The foaming particle of the magnitude of the range of 0.5-10mm diameter In order to reform the front face of the particle so that an interaction may be carried out stably mutually when carrying out mutual homogeneity contact of these, it is given to heat treatment and/or processing with at least one coating. Subsequently It is the manufacturing method of the foaming product made from sufficient long time amount for making the foaming particle condense, and the biodegradability plastic material which consists of holding homogeneity contact mutually.

[0023] The good resilience property of a foaming particle can be borne at any colla tempestade PUSHINGU (cellular destruction) phenomena, when a particle is in homogeneity contact. Coating

which can be used by the approach by this invention For example, i. Water of the liquid which may add a salt and/or an additive, or gaseous water, ii. The solution, the water suspension, or the water emulsion of nature or composition, a giant molecule, or the matter of a monomer, or said matter by the melting condition and iii. -- a solvent with wetting power high enough, and iv. Nature or composition in said solvent, a giant molecule or the solution of the matter of a monomer, suspension or an emulsion, and v. The melting point 130 degrees C or less -- desirable -- polymer 90 degrees C or less.

[0024] The example of coating which can be used for a solution, suspension, or an emulsion water by the approach of this invention -- Pori (vinyl acetate), -- Pori (vinyl butyrate), vinyl acetate, or vinyl butyrate and vinyl ester, By the copolymer with the monomer beyond one or it chosen from acrylate, methacrylate, an allyl compound derivative, pyridinium salt, acrylonitrile, acrylamide, vinyl pyrrolidone, vinylpyridine, and vinyl imidazole Aliphatic series polyester [like -- poly caprolactone by which a part or all may be hydrolyzed] these [whose] are or a lactic-acid polymer, graft-ized Pori (vinyl acetate), or Pori (vinyl butyrate), -- Pori as for which refining was carried out by Pori (vinyl alcohol) which may mix conditioning with a plasticizer and/or boric acid, borate, and a gelling agent like titanate, -- acetalization, etherification, or esterification at high or the rate of low hydrolysis (vinyl alcohol)

-- The block copolymer of Pori (vinyl alcohol) with Pori (vinyl acetate or styrene), -- Pori (vinyl alcohol) of a fatty-acid cap, a polyoxyethylene and/or polyoxypropylene, and graft-ized Pori (vinyl alcohol), -- Oxidation the natural starch of all the origins, hydroxyalkyl-izing, and cationicity -- The starch by which refining was carried out by the starch constructed [the bridge] for which and hydrolyzed or ester, the ether, and/or the phosphoric-acid radical, -- Casein and caseinate, alkyl cellulose, a hydroxyalkyl cellulose, and cellulose ester, For example, the cellulose acetate and the carboxymethyl cellulose by which refining may be carried out with plasticization and/or aliphatic series ester like a caprolactone, -- Natural rubber like natural rubber latex, -- acrylamide, acrylonitrile, styrene or acrylic ester, and the gum Arabic that may be graft-ized (vegetable hydrocolloid), -- An alginic acid, alginate, an abietic acid, rosin resin, an agar, GUYAGAMU, KARAGININ, xanthene rubber, a pullulan, chitosan, a shellac, animal gelatin, A protein, an emulsifier, a dispersant, a bulking agent, -- Pori (acrylic acid), ethylene / acrylic-acid copolymer, Ammonium or sodium salt of acrylamide / acrylic-acid copolymer, and the ionicity polymer guided from Pori (styrene sulfonic acid), Generally -- The gay and copolymer, especially the poly caprolactone of a property of aliphatic series, Those copolymers with polyurethane like Pori (lactic acid), Pori (hydroxy butyrate BARETO), and Pori (butanediol succinate), a polyamide, polyester, and the polyfunctional alcohol permuted selectively.

[0025] In the matter mentioned above, especially Pori (vinyl acetate) is suitable for the activity as coating by the approach by this invention. As for the manufacturing method of the foaming product of this invention, it is desirable to continue simultaneous before a homogeneity contact **** process, and to consist a particle of heat and/or a process which carries out aeration processing because of acceleration of polymerization-izing of the monomer matter contained in evaporation and/or coating of the liquefied matter.

[0026] It is suitable to present back desiccation processing with the foaming product obtained further. After this, desiccation processing can make the water or the solvent which remains able to remove, and can be performed under desiccation, humidity, or the conditions that were adjusted. a polymer -- in the case of coating which consists of a monomer [-izing / a monomer], a polymerization reaction and/or particle condensation can use said after treatment for a completion **** sake. Furthermore, said back desiccation processing phase can stabilize the configuration of the product obtained.

[0027] the case where coating is used with an emulsion gestalt -- the range of 0.05 -- 3wt% -- desirable -- the range of 0.1 -- 2wt% -- more -- desirable -- An emulsifier and/or a thickener can be included in the amount of the range of 0.2 -- 1wt%. the emulsifier which can be used -- for example, -- 3-25 -- desirable -- It is a surfactant with the hydrophilic property / oleophilic balance characteristic of the range of 6-20 (HLB). what esterified the polyoxyethylene (4-20 mols) which esterified a polyoxyethylene or polyoxypropylene in the effective surface active agent especially with what was directly esterified with the fatty acid, for example, a lauric acid, a palmitic acid, or stearin acid, or polyoxyethylene-ized sugar with the fatty acid -- for example, -- the oxy-ethylation (4-20 mols) sorbitol esterified with the 1-6-mol fatty acid, and ** -- there is a

thing of induction from a polyoxyethylene or polyoxypropylene. [like] Furthermore, the surface active agents which can be used are the polyoxyethylene ether with oxy-ethylation nonyl phenol, the lanolin ether and ester, triethanolamine oleate and the poly glycol ester of a fatty acid, for example, stearyl alcohol, cetyl alcohol, or fatty alcohol like cholesterol and PEG-beef tallow amide, and PEG-castor oil.

[0028] The thickeners which can be used are carboxymethylcellulose sodium, methyl cellulose, natural rubber, clay, etc. According to the desirable mode, the approach of this invention can be suitably performed by using the format of equipment as shown in drawing 1 . In drawing 1 , the citation numbers 1, 3, and 9 operate by the compressed air respectively by the closing motion system which shows the separation wall which can be slid and is shown by 2, 4, and 10.

[0029] The separation wall 1 is opened and a measuring chamber 5 is filled up with a foaming particle. Subsequently, the separation wall 1 is shut, the separation wall 3 is opened, and a particle is entrapped to an atomizing chamber 6. subsequently, enough to shut the separation wall 3, start actuation of the sprayer 7 containing coating, and saturate an atomizing chamber 6 with coating -- long -- time amount actuation is carried out. A sprayer 7 is stopped here, the separation wall 9 is opened, and a particle is entrapped into a duct 11. The parts 14 and 15 of a mould which are a male and a female respectively are held in such a location. The width of face of the air spacing 16 in the meantime is smaller than the diameter of a pellet. The separation wall 9 is shut, a particle is supplied to a mould side with a piston 12, and a pressure is put on them. Finally a mould is opened with a piston 17 and the products obtained are collected.

[0030] According to another desirable mode, the approach of this invention can be suitably performed by giving a supply path to the molding room of the same equipment (mould with aeration puncturing) with having used for sintering a form polystyrene particle, and giving a **** and a foaming particle to processing with coating directly. Finally, coating can supply a foaming particle suitably directly through the hole of a mould after filling up a mould.

[0031] The following example is not given for the purpose of instantiation, and does not limit this invention.

The trial of characterization resilience ***** measures the ingredient engine performance recovered to the initial form, after adding the load which brings about deformation.

[0032] Diameter 125mm and height A 150mm cylinder container is filled up with a foaming particle, the flat sensor of a load cell is pushed in, and it is made to operate the rate for 25mm/. A sensor pushes a particle in 33% of cylinder height, and, subsequently to a start location, returns a sensor. A sensor performs 2nd particle compression actuation by the same actuation as the 1st time after 1 minute. The resilience value reported for a% of numeric value is 100 times the ratio which broke the load of the 1st compression actuation by the load of the 2nd compression actuation.

Consistency Dapp (kg/m³) The ** (appearance) consistency of the foaming particle computed from the weight of 5l. of particles, and Dbulk (kg/m³) The specific gravity consistency of each foaming particle, and Dexp (kg/m³) Specific gravity consistency of a foaming product.

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EXAMPLE

[Example]

Example 1 mixture was made from the following constituents.

– potato starch Pori (vinyl alcohol) 10wt% and water of 75wt% and 86% of rates of hydrolysis 15 – wt % -- this -- a constituent -- a diameter -- (– d –) -- 30 -- mm -- die length -- a diameter -- a ratio -- [– (– L –) – / – (– d –) –] -- 30 -- a twin screw extruder -- APV2030 was supplied. The operating condition was performed as follows.

[0034] – Screw rotational speed 150rpm and temperature gradient 69 degree-C/100 degree-C/180 degree-C/170 degree-C/155 degree C and extrusion outlet It adjusted so that 10kg [/] all moisture content might be held to about 14% an hour. the obtained pellet -- mean-particle-diameter abbreviation 1.5 micrometers Talc 0.5 -- % -- a diameter -- (– d –) -- 40 -- mm – [– (– L –) – / – (– d –) –] -- 28 -- a monopodium -- a screw extruder -- ex OMC supplying -- diameter (d) 0.8 mm and [(L)/(d)] It equipped with the extrusion head of one or less nozzles [four].

[0035] The operating condition was performed as follows.

– Screw rotational speed 40rpm and temperature gradient 80 degree-C/120 degree-C/190 degree-C/190 degree-C/200 degree C and extrusion outlet 52kg/hour and head cutting cutting-edge rotational speed The pellet of the charge of 4000rpm foam was obtained. A property is shown in a table 1.

[0036]

[A table 1]

An example Particle size Dapp Dbulk Resilience (mm) (kg/m³) (kg/m³) (%) 1 3.5 15 32 65 2 3.0 10 21 71 3 3.2 14 2875 4 3.3 21 39 65 5 3.2 16 35 68 6 3.5 21 40 58 example 2 operating instructions presupposed that it is the same as that of an example 1, and used the mixture of the following constituents.

[0037] – potato starch 64wt% and 99.8% of rates of hydrolysis, molecular weight (Mw) 70,000, and an ethylene unit -- 44-mol % -- included EVOH 25wt% and water 10wt% – glycerol mono-olate 1wt% -- the moisture content in a pellet was about 10%. The property of a foaming pellet is shown in a table 1.

Example 3 operating instructions presupposed that it is the same as that of an example 1, and used the mixture of the following constituents.

[0038] – potato starch 78wt% and 99.8% of rates of hydrolysis, molecular weight 70,000, and an ethylene unit -- 44-mol % -- Pori (vinyl alcohol) of EVOH 7wt% and 86% of included rates of hydrolysis 8wt% and water 6wt% – glycerol mono-olate 1wt% -- the moisture content in a pellet was about 12%. The property of a foaming pellet is shown in a table 1.

Example 4 operating instructions presupposed that it is the same as that of an example 1, and used the mixture of the following constituents.

[0039] – potato starch 68wt% and poly caprolactone (UC PCL 787) 10wt%, caprolactone-urethane block-copolymer (Pellethane 2102-85AE9) 5wt%, and water 15wt% – glycerol mono-olate 1wt% -- the moisture content in a pellet was about 10%. The property of a foaming pellet is shown in a table 1.

Example 5 operating instructions presupposed that it is the same as that of an example 1, and used the mixture of the following constituents.

[0040] – potato starch Ethylene-acrylic-acid copolymer (Dow Chemical Co. make) which

includes 75wt% and an acrylic unit for 20-mol % 10wt% and water 15wt% -- the moisture content in a pellet was about 10%. The property of a foaming pellet is shown in a table 1.

Example 6 operating instructions presupposed that it is the same as that of an example 1, and used the mixture of the following constituents.

[0041] - potato starch Substitutional rate plasticized at 75wt% and caprolactone 20% Cellulose acetate of 2.5 10wt% and water 15wt% -- the moisture content in a pellet was about 12%. The property of a foaming pellet is shown in a table 1.

The measuring chamber 5 of the equipment shown in example 7 drawing 1 , capacity The foaming particle obtained by 2l. in the example 3 was supplied.

[0042] Subsequently, it processed by the VINABIRU (Vinavil) NPC emulsion (Enichem Systhesis) which contains Pori (vinyl acetate) 50% by the above-mentioned approach, and atomized with the sprayer 7. Back desiccation processing was performed to the reaction chamber which controlled the obtained manufacture to 23 degrees C and (relative humidity RH) 30% for 15 hours.

[0043] The property of a foaming product is shown in a table 2.

[0044]

[A table 2]

An example Mould temperature Dexp Longitudinal shrinkage (degree C) (kg/m3) (%) 7 20 50 3 8

20 43 3.5 9 20 40 4 10 20 36 511 20 25 1 12 20 60 23 13 30 4612 Example 8 operating instructions presupposed that it is the same as that of an example 7. At this time, it is dilution with the water of a VINABIRU (Vinavil) NPC emulsion (Enichem Systhesis). It could be 1/10 (water/Vinavil).

[0045] The property of a foaming product is shown in a table 2.

Example 9 operating instructions presupposed that it is the same as that of an example 7. At this time, it is dilution with the water of a VINABIRU (Vinavil) NPC emulsion (Enichem Systhesis). It was referred to as 1/5 (water/Vinavil).

[0046] The property of a foaming product is shown in a table 2.

Example 10 operating instructions presupposed that it is the same as that of an example 7. At this time, it is dilution with the water of a VINABIRU (Vinavil) NPC emulsion (Enichem Systhesis). It was referred to as 1/2 (water/Vinavil).

[0047] The property of a foaming product is shown in a table 2.

Example 11 operating instructions presupposed that it is the same as that of an example 10, and a different point used what was obtained from the example 2 for the foaming pellet. The property of a foaming product is shown in a table 2.

Example 12 operating instructions presupposed that it is the same as that of an example 10, and a different point used what was obtained from the example 1 for the foaming pellet.

[0048] The property of a foaming product is shown in a table 2.

Example 13 operating instructions presupposed that it is the same as that of an example 10, and a different point performed back desiccation processing in 23 degrees C and the reaction chamber controlled to RH55% for 15 hours. The property of a foaming product is shown in a table 2.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the schematic diagram of the equipment in which the manufacturing method of this invention is shown.

[Description of Notations]

- 1 Separation Wall
- 2 Closing Motion System
- 3 Separation Wall
- 4 Closing Motion System
- 5 Measuring Chamber
- 6 Atomizing Chamber
- 7 Sprayer
- 9 Separation Wall
- 10 Closing Motion System
- 11 Duct
- 12 Piston
- 13 Shaping Room
- 14 Male Mould
- 15 Female Mould
- 16 Air Gap
- 17 Piston

[Translation done.]

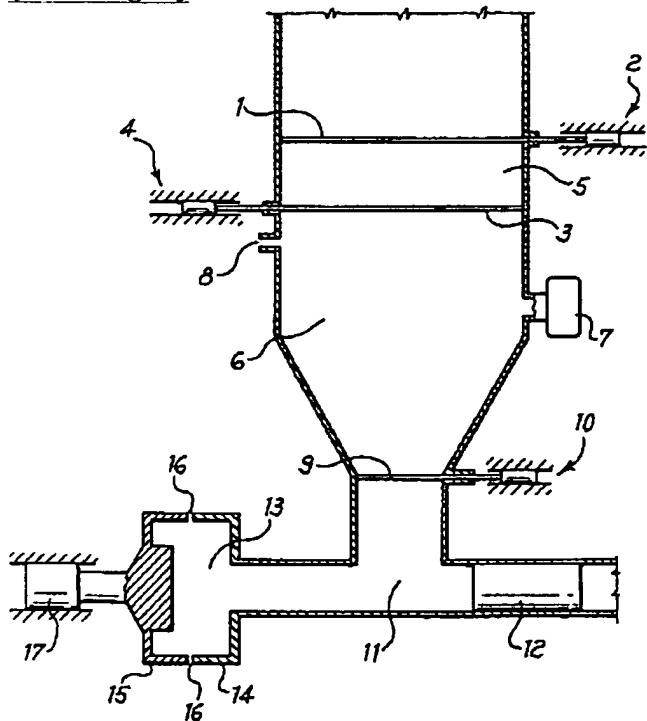
* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DRAWINGS

[Drawing 1]



[Translation done.]